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SHORT COMMUNICATION

COLOURING MATTERS FROM *PRISMATOMERIS MALAYANA*

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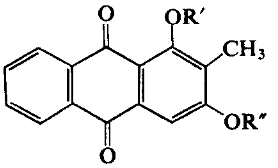
Abstract—Two pigments isolated from the roots of *Prismatomeris malayana* have been shown to be rubiadin-1-methyl ether and rubiadin respectively.

Prismatomeris malayana (Rubiaceae) belongs to a small genus of shrubs indigenous to Western Malaysia. Aqueous extracts of its yellow root-shavings were reported to be used as an adjunct in dart poison.[1] The present work is limited to the investigation of two pigments isolated from the roots of the plant.

The methanolic extracts of the roots on concentration afforded a yellow compound, m.p. 293–295°, with light-absorption (Table 1) indicative of a substituted anthraquinone.[2] It was identified as rubiadin-1-methyl ether (I) by comparison of its i.r. spectrum and that of its derivative (II), obtained by methylation with diazomethane, with published spectra.[3] The NMR spectrum of II (Table 2) was also consistent with the known structure.



(I) $R' = CH_3, R'' = H$
(II) $R' = R'' = CH_3$
(III) $R' = R'' = H$
(IV) $R' = H, R'' = CH_3$

Preparative TLC of the mother liquor yielded, in addition to I, another yellow compound, m.p. 300°, identified by its i.r. spectrum[3] as rubiadin (III). Whereas methylation of rubiadin (III) with dimethyl sulphate gave II, treatment with diazomethane afforded instead IV, with an NMR spectrum (Table 2) in agreement with the assigned structure. The formation of IV is also consistent with the reported resistance of chelated hydroxyl groups to methylation by diazomethane.[4]

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[1] I. H. BURKHILL, *Dictionary of the Economic Products of the Malay Peninsula*, Vol. II, p. 1808, Crown Agents, London (1935).

[2] A. I. SCOTT, *Interpretation of the Ultraviolet Spectra of Natural Products*, p. 286, Pergamon Press, Oxford (1964).

[3] H. BLOOM, L. H. BRIGGS and B. CLEVERLEY, *J. Chem. Soc.* 178 (1959).

[4] R. ROBINSON and K. F. TSENG, *J. Chem. Soc.* 1004 (1938).

TABLE 1. LIGHT-ABSORPTION OF RUBIADIN AND DERIVATIVES

	λ_{max} in nm (log ϵ)	
Compound	95% EtOH (acidic)	95% EtOH (alkaline)
Rubiadin-1-methyl ether (I)	238 (4·26)	247 (4·42)
	244 (infl. 4·23)	314 (4·40)
	282 (4·55)	480 (3·72)
	358 (3·48)	
Rubiadin dimethyl ether (II)	239 (4·18)	
	245 (4·17)	
	276 (4·55)	
	350 (3·63)	
Rubiadin (III)	242 (infl. 4·35)	270 (4·41)
	246 (4·40)	315 (4·48)
	282 (4·46)	512 (4·02)
	335 (3·36)	
	412 (3·84)	
Rubiadin-3-methyl ether (IV)	240 (infl. 4·31)	261 (4·50)
	245 (4·34)	284 (infl. 4·14)
	276 (4·45)	315 (infl. 3·61)
	334 (3·42)	395 (3·35)
	410 (3·79)	510 (3·76)

TABLE 2. NMR SPECTRAL DATA OF RUBIADIN METHYL ETHERS. ($CDCl_3$, 60 Mc) IN ppm FROM TMS

Assignment	(II)	(IV)
1–OCH_3	3·94 (s)	*
2–CH_3	2·26 (s)	2·12 (s)
3–OCH_3	4·04 (s)	4·00 (s)
4–H	7·67 (s)	7·35 (s)
5, 8–H	7·80 (m)	7·80 (m)
6, 7–H	8·32 (m)	8·32 (m)

s = singlet; m = multiplet.

* An acidic proton signal appeared at 13·0 ppm which partially exchanged with D_2O on shaking.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot-stage apparatus. Light absorption spectra were measured with a Perkin-Elmer model 137 u.v. spectrophotometer. Microanalyses were by Mrs. H. K. Tong (Singapore).

*Isolation of Rubiadin-*1*-methyl Ether and Rubiadin*

Ground root of *Prismatomeris malayana* (1 kg) was first defatted by continuous extraction (24 hr) with light petroleum (b.p. 60–80°) and then extracted continuously with methanol (2 l.) for 72 hr. The methanolic solution was concentrated to *ca.* 300 ml and filtered to remove a yellow solid (8 g) which, after two recrystallizations from ethanol, gave pure rubiadin-1-methyl ether as yellow needles, m.p. 293–295° (lit.,[5] m.p. 290–291°) (Found: C, 71·5; H, 4·5. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5 per cent). A suspension of rubiadin-1-methyl ether in methanol on standing overnight with an excess of diazomethane in ether gave rubiadin dimethyl ether which crystallized from benzene–petroleum ether (60–80°) as yellow needles, m.p. 160–161° (lit.,[5] m.p. 159–161°) (Found: C, 71·9; H, 5·1. Calc. for $C_{17}H_{14}O_4$: C, 72·3; H, 5·0 per cent).

The mother liquor on evaporation gave a mixture of solids (3 g) which was found by TLC (Merck Kieselgel H) in benzene:methanol:acetic acid (45:8:4) to consist of two pigments with the slower-moving pigment being rubiadin-1-methyl ether. A portion of the mixture (1 g) was separated by preparative TLC and gave rubiadin-1-methyl ether (520 mg), and rubiadin (270 mg) which crystallized from acetic acid as yellow plates, m.p. 300° (lit.,[6] m.p. 302°) (Found: C, 70·6; H, 4·2. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 4·0 per cent), diacetate, m.p. 236–237° (lit.,[6] m.p. 235°) (Found: C, 67·5; H, 4·4. Calc. for $C_{19}H_{14}O_6$: C, 67·5; H, 4·2 per cent). Rubiadin was converted to its dimethyl ether by dimethyl sulphate in refluxing acetone solution in the presence of anhydrous potassium carbonate. A suspension of rubiadin in methanol after standing overnight with excess diazomethane in ether gave rubiadin-3-methyl ether which crystallized from ethanol as orange–yellow needles, m.p. 189–191° (lit.,[7] m.p. 186°) (Found: C, 71·6; H, 4·7. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5 per cent), ν_{max} ($CHCl_3$) 1670, 1630, 1595, 1575, 1490, 1465, 1415, 1365, 1330, 1305, 1295, 1280, 1145, 1045, 1015, 930 and 870 cm^{-1}.

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[7] E. T. Jones and A. Robertson, *J. Chem. Soc.* 1699 (1930).